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(21) International Application Number: PCT/US91/06470 (22) International Filing Date: 9 September 1991 (09.09.91) (30) Priority data: 583,129 17 September 1990 (17.09.90) US (71) Applicant: MOTOROLA, INC. [US/US]; 8000 West Sunrise Blvd., Ft. Lauderdale, FL 33322 (US). (72) Inventors: DAVIS, James, L. ; 8165 N. University Drive #52, Tamarac, FL 33321 (US). PENNISI, Robert, W. ; 334 N.E. 5th Street, Boca Raton, FL 33432 (US). NOU-NOU, Fadia ; 1321 N.W. 70th Avenue, Plantation, FL 33313 (US). LANDRETH, Bobby, D. ; 614 S.W. 18th Street, Fort Lauderdale, FL 33315 (US).		(74) Agents: NICHOLS, Daniel, K. et al.; Motorola, Inc., Intellectual Property Dept., 8000 West Sunrise Blvd., Ft. Lauderdale, FL 33322 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: SOLDER PASTES CONTAINING ACRYLIC ACID AND DERIVATIVES THEREOF (57) Abstract Solder pastes having vehicles including acrylic acid, polyacrylic acid and derivatives thereof as fluxing agents, rheological aids or both are described. As a fluxing agent the materials clean oxides from the pointed circuit boards (PCBs) under assembly and then volatilize leaving little or on undesired residue. The polymeric materials unzip or decompose to harmless and often volatile materials. The residue, if any, may be completely removed by washing with formic acid. Such fluxing agents can be mixed with typical solder components, such as lead/tin solder pastes, or applied topically to solders, such as solder balls; both techniques permit the assembly of PCBs more easily with high quality bonds, and with little or no residue. Useful polymeric derivatives of acrylic acid include, but are not limited to, polymethacrylate, polyacrylamide, poly(methyl methacrylate) and polyacrylonitrile.		

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SOLDER PASTES CONTAINING ACRYLIC ACID AND DERIVATIVES THEREOF

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Cross-References to Related Applications

This application is related to U.S. patent application Serial No. 07/524,540, filed on May 17, 1990, by Davis, et al, and assigned to Motorola, Inc., which relates to solder flux formulations containing malic acid; and is related to U.S. patent application Serial No. 07/583,630, filed on September 17, 1990, by Davis, et al, and assigned to Motorola, Inc., which relates to methods of using solder pastes that leave residues that may be cleaned by formic acid.

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Field of the Invention

The invention relates to solder paste formulations, and in one aspect, more particularly relates to solder paste formulations that contain acrylic acid, polyacrylic acid and/or derivatives thereof.

30

Background of the Invention

Solder formulations, also known as solder creams or solder pastes, are homogeneous blends of a soft solder alloy typically in a powder form dispersed in a liquid medium conventionally containing a fluxing composition or flux, an organic solvent, and a thickening agent which will give the desired viscous or paste-like consistency to the solder formulation. Such solder formulations can be applied to the surfaces or locations in a number of various ways, such as by

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screen printing, or by means of a dispenser such as a syringe, or simply by dipping the site to be soldered into the solder paste formulation so that the viscous paste adheres to the site, such as an electronic component lead.

5 Recently, solder paste formulations have been used increasingly by the electronics industry, particularly in the automated manufacture of printed circuits in which leadless miniature electronic components are surface mounted on a printed circuit board (PCB) to which a solder paste formulation
10 has previously been applied, such as by screen printing. The PCB is then subjected to a sufficiently high temperature, for example by means of a heated conveyor belt, to cause the flux and solder alloy in the formulation to liquefy and contact the electronic component leads so that on subsequent cooling of the
15 PCB, the components will remain soldered on the PCB.

 The rheological properties of the solder paste dictate the screen printability of the material. Hence, in order to obtain good line definition on the PCB, the rheology of the paste must fall within a relatively narrow process window. Solder paste
20 rheology is largely determined by those components of the solder paste which are collectively known as the vehicle. Generally, solder paste vehicles consist of solvents to dissolve the rosin fluxes or fluxing agents and the activators, and other additives to achieve the proper rheology. Currently,
25 cyclohexanol (sorbitol) derivatives and various Cellosolve™ mono- and dialkyl ethers of ethylene glycol and derivatives thereof are used in commercial solder pastes. Problems encountered with conventional solvents include poor solubility of the organic acid fluxing agents in the solvents which is
30 sometimes addressed by using more solvent that is considered desirable, and an inability to obtain high viscosities (poor rheological control).

 For some uses in the electronics industry, it is desirable to use as the flux composition of the solder formulation a material
35 which is non-corrosive and which will provide, after the heating and cooling steps, flux residues which are themselves

non-corrosive and non-conducting. For this reason, rosin-based flux compositions are widely used in the commercially available solder paste formulations specifically made for use in the manufacture of surface mounted electronic components.

5 Alternatively, more reactive fluxing compositions may be used, which leave residues which are corrosive and/or conductive. Often a somewhat corrosive fluxing composition is desired so that the oxides which form on the metal surfaces to be soldered may be removed to permit the subsequently formed
10 solder bond to be stronger both physically and electrically. Corrosive fluxing compositions usually leave residues and it is necessary to remove these residues formed by means of either aqueous or organic solvent systems to ensure that the resulting soldered circuit is noncorrosive.

15 The use of solder paste formulations containing such rosin-based or more reactive fluxes has a number of disadvantages. First, because the noncorrosive residues (such as rosins) tend to be sticky, they prevent repetitive automatic testing of the circuit. Rosin based fluxes tend to leave copious
20 amounts of residue on the circuit. Additionally, such residues are unsightly and therefor, as with the corrosive flux residues which are also unattractive, will need to be removed. The removal step involves extra production equipment, time and material.

25 Secondly, flux residues tend to be hygroscopic and may thereby cause spattering. Thirdly, some fluxes permit solder particles in the paste to move away from the solder site and give rise to the formation of numbers of discrete small balls of soft solder around the soldered joints, which can create electrical
30 short circuits.

 Because of these and other disadvantages, it is desirable and often essential to meet specifications, to remove the flux residues and any solder balls as much as possible. Often, however, their removal is difficult or impossible, particularly
35 from areas of the PCB underneath the electronic components.

As noted, a common procedure is to use an aqueous or organic solvent in the removal of flux residues. Though water is preferred because it will not leave an objectionable residue itself, water typically is an ineffective agent, since many of the
5 residues, such as the rosin residues, are only slightly soluble in water. Organic solvents are more effective, but less desirable because they are more expensive and particularly because they are more troublesome to dispose of. A particular class of organic solvents that had attained widespread use was the halocarbons,
10 such as the chlorofluorocarbons (CFCs), because they would volatilize after cleaning. However, these materials are particularly inert and their eventual decomposition is involved in the undesirable depletion of atmospheric ozone.

Thus, for these and other reasons the prior solder fluxing
15 compositions are less preferred, and it would therefore be advantageous to discover a new fluxing composition that would avoid one or more of these disadvantages. For example, it would be advantageous to provide solder pastes with fluxing agents whose residues could be easily cleanable by a relatively
20 inexpensive organic solvent that is readily disposed of, such as formic acid.

Summary of the Invention

Accordingly, it is an object of the present invention to
25 provide a solder fluxing composition that would provide an oxide removing agent during the soldering process.

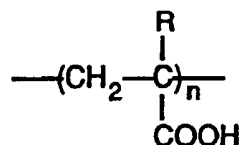
It is another object of the present invention to provide a novel fluxing agent which is an oxide removing agent that would either readily volatilize or be readily removed with a
30 relatively inexpensive organic acid.

It is yet an additional object of the invention to provide a fluxing composition that would accomplish the above objectives, but also be easy to formulate.

Still another object of the invention is to provide a
35 fluxing agent that is a derivative of acrylic acid that will

simultaneously serve to improve the rheological properties of the solder paste formulation.

In carrying out these and other objects of the invention, there is provided, in one form, a solder paste vehicle having a
5 solvent and an additive having the formula:

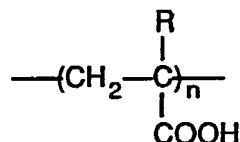


where R is H or lower alkyl and n ranges from 1 to 10,000 ;

where the additive is present in an amount effective to perform a function selected from the group consisting of fluxing,
10 rheology improving and mixtures thereof.

Detailed Description of the Invention

Acrylic acid and polymers and derivatives thereof have been found to be useful additives in solder paste vehicles and,
15 in turn, in solder paste formulations. These materials have the formula:



where R is H or lower alkyl and n ranges from 1 to 10,000.

Lower alkyl is defined as C₁ to C₆.

20 When R is hydrogen and n is 1, this structure is acrylic acid. When R is hydrogen and n ranges from about 2 to about 10,000, the structure represents polyacrylic acid. When R is methyl, the structure represents methacrylic acid and polymethacrylic acid. These materials have shown effectiveness
25 both as a fluxing agent and as a rheological aid.

Polyacrylic acid and acrylic acid have been found to be particularly effective as fluxing agents for lead/tin and lead/tin/silver solders. Some of the other polymeric materials, such as polymethacrylic acid, are expected to be effective fluxing
30 agents as well.

The rheological properties of solder paste dictate the dispensability of the material. Thus, in order to obtain the best line definition, the rheology of the paste must fall within a narrow process window. The higher molecular weight materials of the invention are thus useful as thixotropes and thickeners. In nonaqueous solutions polyacrylic acid and methacrylic acids exhibit viscosity behavior similar to polymethacrylates. It is the viscosities of these nonionic acrylic solutions that make these additives attractive as rheological aids in solder pastes.

Important variables in providing the ultimate rheology of the end product solder paste include, but are not limited to, the process by which the paste is applied, the molecular weight and thixotropic characteristics of the thickener additive, the proportions of thickener used, etc. Thus, while the molecular weight of these polymer additives may range from between about 500 and 20,000, it will be appreciated that these other factors be considered. Because of these interacting factors, it is difficult to define absolute ranges for additive proportions and molecular weights.

There are many advantages to using acrylic based polymers as thickening agents for solder paste. First, they provide good control of solder paste rheology due to the higher viscosities of the polymer solutions. Secondly, the acrylic based polymers listed above do not contain chlorine as some other potential additives might. Hence, the possibility of ionic contamination from the polymer additives is minimized.

Another benefit of methacrylate additives is that they tend to decompose at or near the temperatures used in soldering. Unzipping of acrylic polymers at soldering temperatures occurs rapidly by a chain reaction and produces almost exclusively the monomer. The monomer will either evaporate or decompose to other volatile compounds such as ethylene, propylene, carbon monoxide, carbon dioxide and water. Thus, residues from the thickening agents are expected to be minimal or non-existent due to unzipping and the

subsequent evaporation of the acrylic polymer decomposition products.

The flux of this invention can be prepared in a variety of ways:

- 5 (1) Acrylic acid may be added directly to the solder paste vehicle.
- (2) Polyacrylic acid powder, $-(CH_2CHCOOH)_n-$, or the other polymeric powders may be added directly to the paste vehicle.
- 10 (3) A solution of acrylic acid in a wide variety of solvents including, but not limited to, methanol, ethanol, ethylene glycol, isopropanol and butyl Cellosolve™, is added directly to the solder paste.
- (4) Polymer powders are dissolved in a wide variety of
15 solvents including, but not limited to, methanol, ethanol, ethylene glycol, isopropanol and butyl Cellosolve™, which are then added directly to the solder paste.

In any of these formulations, acrylic acid or polyacrylic
20 acid or other derived species are effective fluxing agents, resulting in solder reflow with minimum residue from the acid. The addition of polyacrylic acid and the other polymers to the paste vehicle is straight forward since the materials are powders. This technology appears particularly attractive since
25 the polyacrylic acid and other materials can function both as a fluxing agent and an additive to obtain proper rheological properties of the paste. The fluxing action of these materials appears to be derived from their ability to reduce surface oxides.

The use of acrylic acid, polyacrylic acid and derivatives
30 thereof will replace current solder fluxing systems based on rosin additives. The addition of either acrylic acid, polyacrylic acid and their derivatives to the solder paste will achieve excellent reflow properties and eliminate the severe residue problems that plague conventional solder pastes. In the case of
35 the thixotropic polymers, rheological improvement will also result.

Typically, the additive is used in the solder paste, or is topically applied to the solder bond to serve as an effective fluxing agent by removing the oxides from the metallic surfaces to which the component is to be bonded. The acrylic acid, polyacrylic acid or other additives are soluble in formic acid so that the formic acid may wash away any residue after the bonding step. It is contemplated, however, that in some embodiments of the invention there will be no residues left and the use of formic acid solvent would be obviated.

The suitable organic acids for the present invention include acrylic acid, CH_2CHCOOH ; polyacrylic acid, $-(\text{CH}_2\text{CHCOOH})_n-$, polymethacrylic acid and mixtures thereof. Polyacrylic acid is preferred in some aspects. Suitable coadditives in combination with those defined above include, but are not necessarily limited to polyacrylamide, poly(methyl methacrylate), polyacrylonitrile and mixtures thereof. In one embodiment of the invention, the polyacrylic acid may have a molecular weight range of from about 100 to about 200,000, and in a more preferred range from about 500 to about 5000.

More specifically, these additives have been found to serve as good fluxing agents for soldering Sn/Pb; Sn/Pb/Ag; and Sn/Pb/Ag/Sb compositions to copper over and above some of the other organic acids. It will be appreciated, however, that other solders are expected to be useful in conjunction with these additives, and that other metals besides copper are expected to be effectively cleaned and bonded to by formulations containing these materials.

With these solder formulations, tests have shown that these acids are effective fluxing agents, resulting in solder reflow bonds having minimum residue, which can be easily removed by formic acid, water or the like. The addition of the polyacrylic acid to the paste vehicle is straightforward since the material is a solid powder at room temperature. Interestingly, acrylic acid and polyacrylic acid can also be used directly or topically as a flux for solder balls or spheres.

The solder used in this process can be untreated solder powder (as in a paste formulation) or solder spheres. The acid may also be applied to formed solder spheres. The metals of the solder may include, but are not limited to lead, tin, antimony, silver and mixtures thereof. These types of solders were found to exhibit excellent reflow characteristics.

In the instances where one of the additives of this invention is used in conjunction with a solvent to provide a vehicle for a solder formulation, in one aspect the proportion of additive in the vehicle ranges from about 0.1 to about 60 wt.% of the vehicle, and in a preferred aspect from about 0.3 to about 40 wt.% of the vehicle.

It will be appreciated that the proportion of additive as a proportion of the solder paste vehicle will vary depending on the particular formulation and its intended use. For example, high temperature solder pastes or pastes for highly oxidized metal surfaces may require a different additive proportion from those outlined above. The minimum amount of additive needed will depend upon the molecular weight of the additive as well. For example, less of a higher molecular weight additive is needed to achieve the same viscosity than if a lower molecular weight additive is used. The balance of the fluxing composition may be any of the customary materials or additives. It will be appreciated that although the other common materials, such as the rosins, may be used in conjunction with the compounds of the invention, that some of these typical materials contribute to flux residues and should not be employed to take full advantage of the little or no residues provided by the flux compositions of the present invention.

Suitable alcoholic solvents for dissolving the acrylic acid and derivatives therefrom include, but are not limited to methanol, ethanol, isopropanol; 2-butanol; 1-hexanol; 1-heptanol; 1-octanol; 1-dodecanol; 2-ethoxyethanol; 2-(2-ethoxyethoxy)ethanol; 2-(2-butoxyethoxy) ethanol; *n*-hexadecanol; *n*-octadecanol; benzyl alcohol; 1,2-ethanediol; 1,2-

propanediol; 1,3-propanediol; 1,2-butanediol; 1,3-butanediol; 1,4-butanediol; 1,2-pentanediol; 1,5-pentanediol; 2,4-pentanediol; 2,5-hexanediol; glycerol; 1,2,4-butanetriol; 2,2'-(ethylenedioxy)diethanol; 1,12-dodecanediol; 1,16-hexadecanediol and mixtures thereof.

The proposed solder pastes containing acrylic acid, polyacrylic acid or other additive can replace current solder fluxing systems based on rosin additives. For example, acrylic acid can replace the acid in conventional abietic acid-based fluxes. The addition of acrylic acid to the solder pastes will achieve excellent solder reflow properties and eliminate or reduce the residue problems that plague conventional solder pastes. This lack of residue reduces the need for any board cleaning with ozone-depleting CFCs after solder reflow.

With any of these organic acid fluxes and methods of this invention, no retooling would be required in the existing assembly line. If the process can be one in which no residue remains, then some cleaning equipment may need to be removed. If some residue does remain with certain of these systems, it will further be appreciated that it may be washed away with formic acid or water. Depending on the exact organic fragments from the nonmetallic compounds, the solvent to rinse them may need to be treated as well. Nevertheless, these concerns are appreciably less than those presented by the CFC cleaning agents.

The invention will be described in more detail with respect to the following illustrative examples.

FLUXING AGENTS

30

Examples 1-15

Various organic acids were added, in quantities ranging from about 10 to about 100 mg., to an aluminum pan containing 10 to 15 30-mil diameter solder spheres. A couple of drops of isopropyl alcohol (IPA) were also added to the pans. The pans were heated on a hot plate to temperatures above the melting point of the tin/lead solder spheres. Whether or not the solder

balls coalesced or fused was observed. Coalescence is a measure of whether reflowing of the solder or wetting of the pan occurred. The following organic acids were evaluated.

5

TABLE I — Organic Acid Screening

<u>Example</u>	<u>Acid</u>	<u>Solder ball coalescence occurred?</u>
1	Abietic acid	Yes
2	Adipic acid	Yes
3	Ascorbic acid	Yes
4	Acrylic acid	Yes
5	Citric acid	Yes
6	2-Furoic acid	Yes
7	Malic acid	Yes
8	Polyacrylic acid [av. mol. wt. = 2000]	Yes
9	Acetic acid	No
10	Cyclohexane carboxylic acid	No
11	Formic acid	No
12	Hexanoic acid	No
13	4-Hydroxybutyric acid/Na salt	No
14	Maleic acid	No
15	Oxalic acid	No

Example 16

Polyacrylic Acid Solder Paste Formulation

- A solution of polyacrylic acid having an average
- 10 molecular weight of about 2000 and isopropanol was added to a copper plated pan containing about ten commercially available solder balls. Solder ball reflow resulted in a small amount of residue that disappeared after 10 seconds in a hydrosonic water bath. During the first run, the pan was accidentally dropped
- 15 while the residue was still a liquid. The residue ran off the pan leaving no visible residues.

Example 17
Polyacrylic Acid/Malic Acid Solder Paste

A low residue, formic acid cleanable solder paste was formulated with the following composition.

5	88.0%	Solder powder
	4.0%	Malic acid (Aldrich, 99%)
	1.0%	EDTA
	1.0%	Polyacrylic acid
	5.0%	1-Dodecanol
10	~2.0%	2-(2-Ethoxyethoxy)ethanol — Added because screen printability was poor.

Testing procedure was as follows. The solder paste was placed in copper plated pans and reflowed. When the solder paste reflowed, the pan was removed from the heat. In this case, solvent bleed-out occurred prior to reflow. A formic acid rinse after the pan cooled to room temperature eliminated virtually all residue.

RHEOLOGICAL AIDS

Through the polymer additives of this invention, the rheological properties of the solder paste can be tailored to meet exacting requirements. Surprisingly, the polymeric additives have been found to serve as both fluxing agents, and as thickening agents to achieve proper rheology. In fact, no other thickening agent need be employed. The use of these additives to simultaneously meet rheology and flux requirements is expected to lower the number of processing steps required in solder paste formulations. In addition, by reducing the amount of additives, such as thickeners, required for acceptable screen printing, the residues remaining from the solder paste following solder reflow will be significantly lowered or eliminated.

For optimum performance of the solder paste, all additives in the vehicle should exhibit a boiling point between about 150 and about 350°C., in one aspect from between about 175 and about 270°C. Lower boiling polymers will decompose

and/or evaporate prior to reflow and would not provide effective fluxing action. As noted previously, at about 350°C. or common soldering temperatures the polymers will unzip into only the monomer and harmless components, many or all of which would volatilize. At temperatures around 250°C. approximately 90 to 95% of the polymer has degraded. These decomposition temperatures are dependent upon the type of acrylic acid polymer, its molecular weight and the chain microstructure.

It should be mentioned that the viscosity of these pastes with polyacrylic acid is about 260 cps, whereas without polyacrylic acid the viscosity is about 100 cps.

Example 18

Screen Printability of Malic Acid Solder Paste

The following formulation was prepared:

40.4671 g Solder Powder

0.8582 g Malic Acid

1.6176 g Polyacrylic acid (PAA)/2-(2-ethoxyethoxy)ethanol solution,
(18% PAA)

1.1520 g Saturated malic acid/2-(2-butoxyethoxy)ethanol solution
(primarily solvent)

1.0176 g 2,5-Hexanediol

Additional solder powder (about 5 g) was added to achieve proper viscosity for screen printing. This result may be achieved by adding less hexanediol, on the order of about 1-1.5%. Although the print definition after screening of this material was poor, appearance after reflow was good.

It is apparent that the use of the compounds of this invention provide useful fluxing agents and rheological aids in solder paste vehicles. Acrylic acid and polyacrylic acid are especially useful organic acid fluxing agents that performs surprisingly better than other acids, particularly in leaving low

portions of residue. Additional embodiments of the invention include topical application of the additives to solder bonds, later cleaned away with organic acids, if necessary.

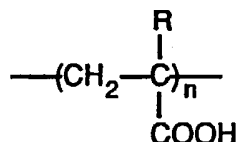
5 It will be appreciated that modifications may be made in the exact implementation of the invention illustrated in the above examples which would still fall within the spirit and scope of the invention as claimed herein. For example, it is anticipated that the processing conditions, modes or sequences of addition of the vehicles and fluxing compositions, and exact
10 combinations of flux components may be altered to optimize the invention by one skilled in the art. It is also expected that the method of this invention could be used to facilitate assembly of PCBs by having solder paste containing the additives screened thereon.

15 The use of acrylic acid derived polymers as thickening agents in solder pastes represents a significant advancement over conventional paste technology, since the polymers possess high viscosities yet decompose to volatile products at soldering temperatures. Thus, acrylic acid derived polymers serve as
20 excellent thickening agents, yet do not produce the large amounts of residues associated with present commercial solder pastes.

Claims

We Claim:

- 5 1. A solder paste vehicle comprising:
 a solvent; and
 an additive having the formula:



- 10 where R is H or lower alkyl and n ranges from 1 to
 10,000; and
 where the additive is present in an amount effective to
 perform a function selected from the group
 consisting of fluxing, rheology improving and
 mixtures thereof.

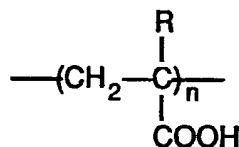
- 15 2. The solder paste vehicle of claim 1 where the
 proportion of the additive in the vehicle ranges from about 0.1
 to about 60 wt.% of the vehicle.

- 20 3. The solder paste vehicle of claim 1 where the
 additive is present as a rheological aid, and whereby the
 additive has a molecular weight between about 100 and 200,000,
 and the proportion of the additive in the vehicle ranges from
 about 0.1 to about 60 wt.% of the vehicle.

- 25 4. The solder paste vehicle of claim 1 where the
 additive is selected from the group consisting of acrylic acid,
 polyacrylic acid, polymethacrylic acid, and mixtures thereof.

30

5. A solder paste formulation comprising:
a solder paste vehicle comprising:
a solvent; and
an additive having the formula:



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- where R is H or lower alkyl and n ranges from 1 to 10,000; and where the additive is present in an amount effective to perform a function selected from the group consisting of fluxing, rheology improving and mixtures thereof; and
a solder powder comprising a metal selected from the group consisting of lead, tin, antimony, silver and mixtures thereof.

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6. The solder paste formulation of claim 5, where the proportion of additive in the vehicle ranges from about 0.1 to about 60 wt.% of the vehicle.

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7. The solder paste formulation of claim 5, where the additive is present as a rheological aid, and whereby n ranges from about 2 to about 500 and the proportion of the additive in the vehicle ranges from about 0.1 to about 60 wt.% of the vehicle.

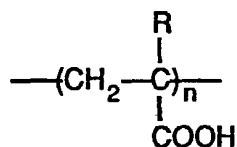
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8. The solder paste formulation of claim 5, where the viscosity of the solder paste formulation ranges from about 100 to about 1000 cps.

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9. The solder paste formulation of claim 5, where the additive is at least one member of the group consisting of acrylic acid, polyacrylic acid, polymethacrylic acid, polyacrylamide, poly(methyl methacrylate), polyacrylonitrile and mixtures thereof.
- 5

10. A method for using acrylic acid or derivatives thereof as a fluxing agent in soldering applications comprising:
applying solder to a metallic surface to be soldered;
topically applying a fluxing agent having the formula:



5

where R is H or lower alkyl and n ranges from 1 to 10,000; and
causing the solder to flow and form a solder bond.

11. A printed circuit board (PCB) bearing solder paste comprising:

an insulative substrate;

5 a plurality of conductive circuit traces on the insulative substrate;

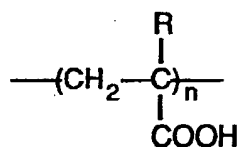
bonding areas on the insulative substrate, where the bonding areas are in electrical contact with the electrical traces; and

10 a solder paste on at least one of the bonding areas, where the solder paste comprises:

a solder paste vehicle comprising:

a solvent; and

an additive having the formula:



15

where R is H or lower alkyl and n ranges from 1 to 10,000; and where the additive is present in an amount effective to perform a function selected from the group consisting of fluxing, rheology improving and mixtures thereof; and

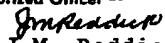
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a solder powder comprising a metal selected from the group consisting of lead, tin, antimony, silver and mixtures thereof.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/US91/06470

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): C09K 3/00; C08K 5/00; B23K 35/00; C08L 33/00 U.S. C1: 106/287.23, 311; 148/22, 23, 24; 524/556		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System ¹	Classification Symbols	
U.S. 106/287.23, 311; 148/22, 23, 24; 524/556		
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	US, A, 3,033,713 (BIELENBERG ET AL) 08 MAY 1962 See entire document.	1-4
Y	US, A, 3,040,781 (REYMAN ET AL) 26 JUNE 1962 See entire document.	1-4
Y	US, A, 3,791,027 (ANGELO ET AL) 12 FEBRUARY 1974 See column 4, line 27, column 6, lines 35 and 36.	1-4
Y	US, A, 3,471,310 (JOSEPH ET AL) 07 OCTOBER 1969 See entire document.	1-4
Y	US, A, 3,832,242 (CUTHBERT) 27 AUGUST 1974 See column 3, lines 20-41, column 4, lines 39-75, column 5, lines 1 and 2.	1-4
A	US, A, 3,895,973 (STAYNER) 22 JULY 1975 See entire document.	1-4
A	US, A, 3,986,899 (KOLE ET AL) 19 OCTOBER 1976 See column 4, lines 49-65, column 5, lines 14-60.	1-4
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁵ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹⁹	Date of Mailing of this International Search Report ²⁰	
21 NOVEMBER 1991	16 DEC 1991	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	 J.M. Reddick	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
A	US, A, 4,113,525 (STAYNER ET AL) 12 SEPTEMBER 1978 See entire document.	1-4
Y	US, A, 4,296,019 (NELSON ET AL) 20 OCTOBER 1981 See entire document.	1-4
Y	US, A, 4,325,754 (MIZUHARA ET AL) 20 APRIL 1982 See entire document.	1-4
A	US, A, 4,541,876 (HWANG) 17 SEPTEMBER 1985 See entire document.	1-4
Y	US, A, 4,554,307 (FARRAR ET AL) 19 NOVEMBER 1985 See column 3, lines 34-62, column 8, lines 34-44, column 9, lines 24-38, column 10, lines 51-58.	1-4
Y	US, A, 4,613,639 (BLUM ET AL) 23 SEPTEMBER 1986 See column 3, lines 13-35, column 7, lines 1-7.	1-4
Y	US, A, 4,762,573 (BIVERSTEDT) 09 AUGUST 1988 See column 1, lines 34-59, column 3, lines 1-45.	1-4
X,P	US, A, 4,995,921 (DAVIS ET AL) 26 FEBRUARY 1991 See column 4, lines 37-46, column 5, lines 1-6.	1-4
A,P	US, A, 5,004,508 (MACE ET AL) 02 APRIL 1991 See entire document.	1-4
Y,P	US, A, 5,037,877 (KERHERVE) 06 AUGUST 1991 See column 1, lines 63-68, column 2, lines 1-68, column 3, lines 1-37.	1-4
Y,E	US, A, 5,064,480 (DERSHEM ET AL) 12 NOVEMBER 1991 See entire document.	1-4
Y,E	US, A, 5,064,481 (DAVIS ET AL) 12 NOVEMBER 1991 See column 4, lines 39-67.	1-4

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____ because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹, specifically:

3. ☐ Claim numbers _____ because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this international application as follows:

- I. Claims 1-4 drawn to a solder paste vehicle classified in Class 524, Subclass 556.
- II. Claims 5-9 drawn to a solder paste formulation classified in Class 524, Subclass 403, 409 and 434.

(See attachment)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers _____ of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international _____ those claims of the international application for which fees were paid, specifically claims:

3. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search _____ the invention first mentioned in the claims; it is covered by claim numbers:
1-4
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

Continuation to Form PCT/ISA/210, Section VI:
ATTACHMENT:

- III. Claim 10 drawn to a method of applying a fluxing agent to a solder applied metallic surface classified in Class 427, Subclass 96.
- IV. Claim 11 drawn to a printed circuit board classified in Class 428, Subclass 901.

The claims of these four groups are directed to different inventions which are not linked as to form a single inventive concept. The Group I invention (claims 1-4) and the Group II invention (claims 5-9) are related as mutually exclusive species in an intermediate - final product relationship. The intermediate product has separate utility from that of the final product such as an adhesive intermediate exclusive of a metal powder. The Group I invention (claims 1-4) and the Group III invention (claim 10) are separate distinct inventions since the method of Group III does not require the solder paste vehicle of Group I but only a portion thereof, namely the acrylic acid. The Group I invention (claims 1-4) and the Group IV invention (claim 11) are related as mutually exclusive species in an intermediate - final product relationship. The intermediate product has separate utility other than that of the final product such as an intermediate in a metal to metal bonding.